Structure of Fluids at Interfaces: A Combined Simulation and Theoretical Study

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Abstract

Understanding the microscopic structure and macroscopic properties of condensed matter from a molecular perspective is important for modern chemistry. The very basis of such understanding is provided by statistical mechanics through bridging the gap between molecular events and the physiochemical properties of macroscopic systems. With ever-increasing computational capabilities, molecular simulations and ab initio calculations hold promise in providing a nearly exact route to statistical mechanics. However, phenomenological and semiempirical methods still remain quite relevant because of their simplicity and versatility in solving complex chemical problems. Under this scenario, amalgamation of analytical theories and computer simulation offers a serious compromise. Recent advances in such methods are summarized with emphasis on quantitative modeling of the interfacial behavior of fluids and soft materials, including simple fluids, colloids, polymer solutions and polyelectrolytes. Attention is also given to some potential applications of these methods to nanomaterials and self-assemblies.

Introduction

The primary objective of statistical mechanics is to interpret and predict the properties of macroscopic systems in terms of their microscopic counterparts. It provides a cornerstone in understanding numerous natural phenomena and for design and optimization of chemical processes. The importance of statistical mechanics in many different branches of basic and applied chemistry has long been realized, although its tunability to specific structural and dynamical problems has become feasible only recently. The obvious reason for such a systematic development is its suitability in covering the entire spectrum of physicochemical problems, thereby providing an inherent proximity to real experimental data. As a corollary, a number of approximate and semiempirical methods emerge which use ingenious combinations of basic concepts from statistical mechanics. The quanta of sophistication in statistical mechanical methods are naturally driven by the specificity of problems used to represent various physicochemical systems. So far, a number of more rigorous theoretical methods have been devised, which are based on molecular simulations, liquid-state theories, Self-Consistent Field (SCF) theory and classical Density Functional Theory (DFT).

The rich variety of equilibrium and dynamical phenomena associated with the solid-fluid interfaces have been a subject of wide variety of research in view of their applications in biological, electrochemical and colloidal nanosystems. In recent years, there has been an upsurge of interest in this field due to significant progress in computer simulation as well as availability of sophisticated tools in theoretical formulations. Most of the earlier developments, however, have been based on simple model systems to mimic the characteristics of the real complex
systems. This article presents some recent developments in the modeling of interfacial properties of fluids and soft materials, carried out in our laboratory. Following a brief introduction to the basic concepts and new developments, the main text is concerned with applications of these methodologies to the interfacial behavior of simple fluids, electric double layers, colloids and structure of polymeric materials. This article concludes with a brief discussion on some possible future applications of theoretical chemistry to fabrication of novel materials, biomolecular engineering and molecular self-assembly.

Basic Concepts and New Developments

Statistical mechanical description of classical systems involves the concept of an ensemble, which is an arbitrarily large collection of imaginary systems, all of which are characterized by the same macroscopic parameters, but each member of the ensemble has different sets of coordinates and momenta of the particles. The system dealing with an interface is an open system in general, and is characterized by fixed values of volume $V$, temperature $T$, and chemical potential $\mu$ with the ensemble designated as a grand canonical ensemble. Theoretical description of classical fluids at an interface starts with the description of the single particle density, $\rho(r)$, of the fluid, conveniently expressed as

$$\rho^{(1)}(r) = \rho(r) = \langle \hat{\rho}(r) \rangle = \left\langle \sum_{i=1}^{N} \delta(r - r_i) \right\rangle$$

The determination of this fundamental quantity has lead to a large number of methodologies, which can be broadly classified, into four categories. The first one is based on the Integral Equation Theory (IET), which has been found to be quite successful in both homogeneous and inhomogeneous forms of description. The second one belongs to methods based on Density Functional Theory (DFT), which have been applied to simple and complex fluids in then various forms of description, viz. perturbative and non-perturbative methods like Weighted Density Approaches (WDA). The hybrid methods that include both the density functional and the integral equation theory constitute the third method, which has been applied quite recently, to study the fluid mixtures and the electric double layer. The fourth one involves the Monte Carlo (MC) and Molecular Dynamics (MD) simulations, which provide direct physical insights into different important aspects of the structure of fluids. The present interest lies mainly in hybrid methods, viz. the Self-Consistent Density Functional Approach (SCDFA) from DFT and IET and the Monte Carlo density functional theory (MCDFT) from MC and DFT. Whereas the former is based on the calculation of density functional quantities from IET and mostly applied to simple fluids including the ionic systems, the latter requires single chain simulation with enumeration of configurations and finds applications in complex polymeric fluids.

Representative Applications

As indicated earlier, there have been numerous applications of the newer theoretical developments and computer simulation methods, to the calculation of various interfacial properties of fluids. Rather than attempting to review the entire work, we have selected only the recent developments in these fields from our laboratory.

Electric Double Layers

The Electric Double Layer (EDL) represents the system of nonuniform ionic fluids originated at the electrode-electrolyte interface and it has direct relevance to many aspects of electrochemistry and biophysics. We have developed a weighted density functional theory, where the only input required is the second order correlation function of the uniform fluid. The calculated ionic density and the mean electrostatic potential profiles compare quite well with the simulation results. Such a study is able to predict the experimental inner layer capacitances ($c_{in}$) quite well as is evident from Fig. 1.

Solvation and Surface Forces
The forces between hydrophobic surfaces immersed in polyelectrolyte solutions is of practical importance such as waste water treatment and protein precipitation. Several experimental measurements have shown, that these forces are oscillatory in nature; this turned out to be attractive in the presence of small amount of salt, whereas excess salt causes the same to become purely repulsive. In the present work, we have proposed a new weighted density approach for predicting the so-called solvation forces in simple liquids. As shown in Fig. 2, it can predict the interaction energies between two mica surfaces immersed in octamethy cyclo tetrasiloxane and liquid tetracdecane, comparable with experimental values.

**Polymers at interfaces**

The structure of polymer melts at interfaces is of immense technological importance in diverse applications such as surface finishing, lubrication, nanotechnology and cybernetics. Theoretical description of polymer molecules starts with united atom model with the two most widely studied are the Freely Jointed Chain (FJC) and the Fused Hard Chain (FHC) models. Among the various theoretical developments, the notable contribution which warrants mention here is the Monte Carlo Density Functional Theory (MCDFT), where it is required to only simulate of a single chain in a self-consistent field, due to the other molecules and surfaces, which is calculated with a prescribed formulation of DFT. Fig. 3 depicts the calculated density profiles of athermal equimolar mixture of polymer and solvent. It is amply clear, that at high polymer density, packing entropic effects force the polymer molecules to pack against the surface. Theoretical developments along the same line for polyelectrolyte systems have predicted many interesting observations for binding interactions including the negative total electrostatic free energy in the presence of multivalent salt.

Fig. 1: The inverse inner layer capacitance for various metals immersed in an aqueous solution against the metallic electron density.

Fig. 2: Interaction energy between two mica surfaces immersed in Octamethyl cyclo tetrasiloxane vs the surface separation.

Fig. 3: Comparison between DFT predictions (lines) and Monte Carlo simulations (symbols) for the density profiles of athermal equimolar mixture of 32-mers and solvent at wall separation $H=10$ and volume fraction $\eta$ as indicated.
Self-assembly of Nanoparticles and Colloids

Self-assembly of large particles into ordered arrays is supposed to be an efficient way of preparing microstructured materials with interesting versatility of desired properties. In the present work, we have carried out a systematic study of the structure and dynamics of self-assemblies, formed from $C_{60}$ fullerene nanoparticles in aqueous solution, by using our molecular dynamics lattice Boltzmann (MD-LB) simulation method. Fig. 4 depicts the structure of $C_{60}$ fullerenes in aqueous solution when coarse-grained MD simulation is carried out. However, representation of accurate solvent correlations through LB simulation leads to $C_{60}$ aggregating into larger clusters as reported in experiments and which can be visualized from Fig. 5.

Concluding Remarks and Future Directions

The contents discussed in the present article are illustrative rather than exhaustive. A number of topics of current interest like the DNA salt binding, the molecular self-assembly, the solvation dynamics, the wetting transition are not covered in the present article. Colloidal macroion in the presence of electrolyte is another fascinating area of R&D. Although much current work in the literature concerns relatively simple models with emphasis on the performance of various versions of the theory for representing the qualitative or semiquantitative physiochemical properties in the bulk or near surfaces, much of it in the coming years will depend upon the development of more realistic intermolecular force fields for more complex systems. Important advances are already emerging in applications of these methods to material fabrication, environmental protection, biomolecular engineering, transport processes through ion channels, and nanotechnology for various highend applications in space, atomic energy and defence equipment. Modeling and simulation will play an extremely crucial role in all these areas of developments for mankind in the foreseeable future!

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Fig. 4: Representative snapshot of 1000 bare $C_{60}$ fullerenes in aqueous solution, volume fraction $f=0.07$ and 298K (water is not shown) after 2 ns in MD simulation.

Fig. 5: Representative snapshot of 1000 bare $C_{60}$ fullerenes in aqueous solution, volume fraction $\varphi=0.07$ and 298K (water is not shown) after 2 ns in combined MD with LB simulation.
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